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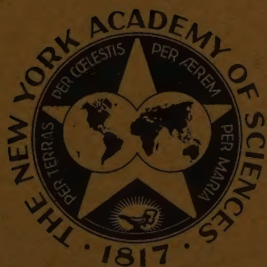
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QUANTUM ASPECTS OF CATALYSIS: THE DRYING OF LINSEED OIL

*By*

RAYMOND R. MYERS



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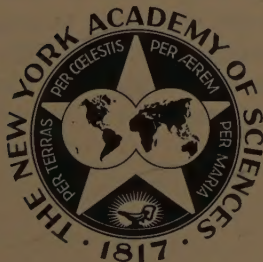
QUANTUM ASPECTS OF CATALYSIS: THE DRYING OF LINSEED OIL

*By*

RAYMOND R. MYERS

*Lehigh University, Bethlehem, Pa.*

Accorded an A. Cressy Morrison Award in Natural Science in 1958  
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# QUANTUM ASPECTS OF CATALYSIS: THE DRYING OF LINSEED OIL\*

Raymond R. Myers  
Lehigh University, Bethlehem, Pa.

## Introduction

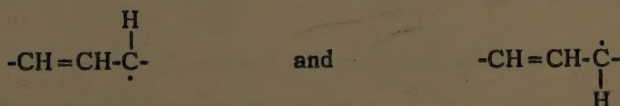
Various explanations of the mechanism of the drying of oleoresinous vehicles have been proposed,<sup>1-3</sup> but few explanations of the role of the catalyst have been advanced.<sup>4,5</sup> The success with which various reactions of a relatively simple molecule such as ethylene have been explained on the basis of quantized transfers of mass<sup>6</sup> has led to a similar study of the more complex reaction of linseed oil with oxygen. This study is described below.

## Mechanism of Autoxidation

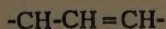
The drying of linseed oil is an oxidation reaction. The precise mechanism by which oxygen attacks the unsaturated molecule need not be considered here, provided that it is agreed that the attack is centered on the alpha methylenic carbon (that is, the carbon adjacent to a  $-C=C-$  group). The free radical nature of the reaction has been fairly well established.<sup>3</sup>

One satisfactory explanation of the reactivity of the alpha carbon is based on the concept of resonance forms proposed by Pauling and Wilson.<sup>7</sup> According to this quantum mechanical view, if a reaction can proceed through two different intermediates, that intermediate is favored for which the greater number of resonance forms can be written.

In the case of the  $-CH=CH-CH_2-$  segment in linseed oil, two possibilities exist for the loss of an alpha hydrogen, both of which produce a radical capable of existing in two resonance forms:

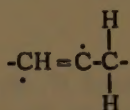


either of which can be considered to be in equilibrium with the radical



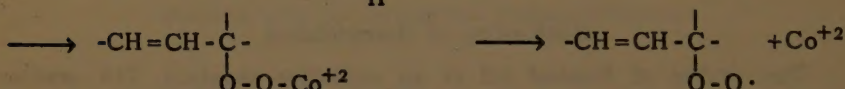
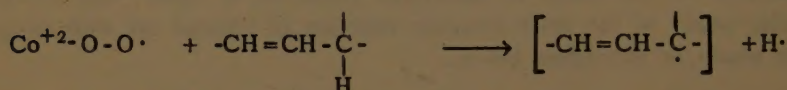
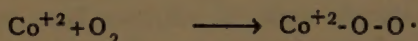
by a shift of the double bond. In comparison, the loss of a hydrogen from a doubly bound carbon produces only

\*This is the second of a series of papers on the quantum aspects of catalysis.<sup>6</sup>



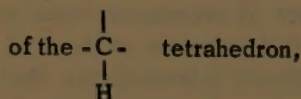
with no possibility of resonance stabilization. Therefore, the alpha methylenic radical appears to be a more likely intermediate.

The role of the catalyst is clarified by these considerations because the metallic driers usually employed are capable of undergoing the following reversible oxidation, exemplified by the cobalt ion:



(While attached to oxygen, the Co ion may be viewed as existing in the trivalent state).

In accordance with the principles presented in the first paper of this series,<sup>6</sup> a correlation will be sought between the vibration frequency of the metal oxide and the vibration mode of the alpha carbon group, that is,



which is reasoned to be most potent in the formation of the free radical. According to the hypothesis the two vibration frequencies should coincide in order to facilitate the transfer of oxygen from the catalyst intermediate and the free radical.

#### *Vibration Modes of the Carbon Tetrahedron*

Two approaches may be used in the assignment of frequencies for the various vibrations of the tetrahedron that encompasses the alpha carbon. One method is to assign modes such as stretching and bending to the infrared absorption frequencies and to search for coincident vibrations. This method has been applied successfully in this study, but details of the mechanism involved are best revealed through the use of a model. Consequently, the second alternative was chosen: namely, an approximation to the linseed oil molecule was made in order to use a model whose vibrational modes were available in an easily visualized form.



Methyl chloride was selected as the model. The bulky halogen replaces the  $\text{-CH=CH-}$  group and the portion of the molecule to the left of it. The replacement of the organic tail by a chlorine atom meets most of the requirements of a model for linseed oil, such as mass, rigidity, volume, and electronegativity. In addition, the fortunate circumstance exists that the vibrational mode selected for consideration concerns the motion of carbon and hydrogen atoms relative to each other rather than relative to the rest of the molecule; therefore, the frequencies in the model should be nearly identical with those of the more complex linseed oil.<sup>8</sup>

The most important aspect of the reaction is that the conversion of the tetrahedron to the free radical results in an intermediate with only three bonds to the central carbon atom. In terms of modern views of chemical bonding,<sup>9,10</sup> this loss of one bond converts the structure from one requiring  $s$  and  $p$  orbitals (the  $sp^3$  hybrid) to one requiring only three  $p$  orbitals. The geometry of the  $p^3$  structure is a cube,<sup>11</sup> rather than a tetrahedron. This simplified picture is important in the discussion which follows, where for various reasons the  $p^3$  configuration is referred to as a pyramid. These structures are shown in FIGURE 1.

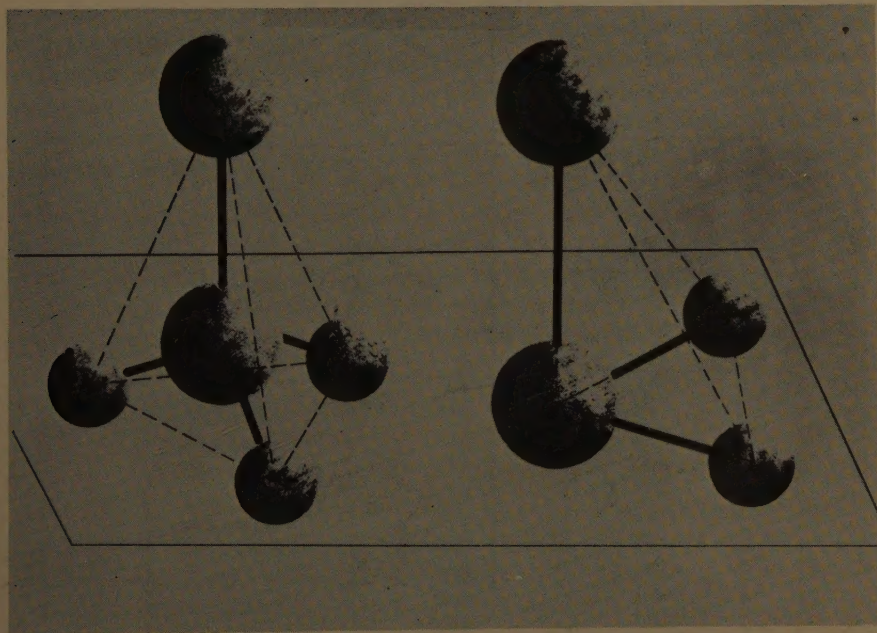


FIGURE 1. Geometric representation of free radical formation.

In order to pass from the tetrahedron to the pyramid that represents the free radical, a bending of the  $\begin{array}{c} \text{C}-\text{H} \\ | \\ \text{H} \end{array}$  group must accompany the loss

of hydrogen. In order to lose one of the hydrogens, a certain amount of bond stretching is required. Herzberg<sup>8</sup> points out that the characteristic bending frequency of the methylene group is  $1450 \text{ cm}^{-1}$ ; therefore one would expect to find the vibration frequency of the catalyst in this region.

FIGURE 2 depicts the 6 vibration frequencies (of which 3 are twofold degenerate) of methyl chloride and illustrates the principle that certain modes can be viewed as specific for a given reaction. For example, vibrations  $\nu_1$  and  $\nu_2$  are C-H stretching modes;  $\nu_5$  represents an oscil-

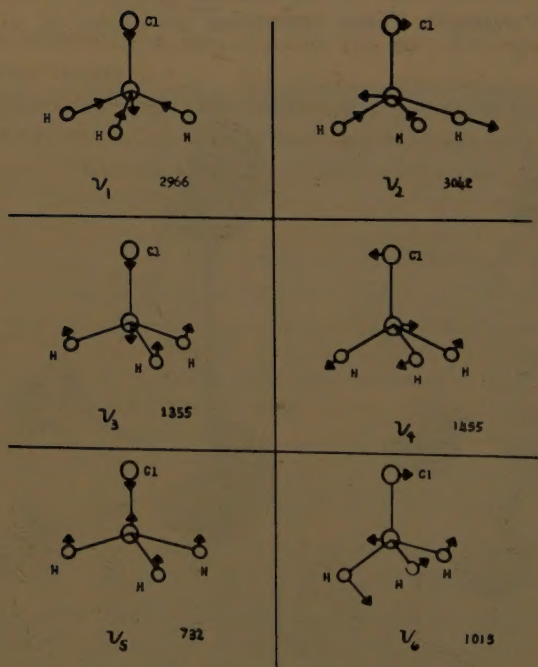


FIGURE 2. Modes of vibration of methyl chloride.



lation of a rigid methyl group with respect to the rest of the molecule, while  $\nu_6$  is a rocking of the same group. The remaining  $\nu_3$  and  $\nu_4$  modes are true deformations, of which only  $\nu_4$  possesses the asymmetry necessary to permit: (1) the change in bond angle from  $109^\circ$  (tetrahedron) to  $90^\circ$  (pyramid), (2) the loss of one hydrogen, and (3) the emergence of the carbon atom from the center of the tetrahedron to a corner of the pyramid (FIGURE 1).

The frequency of the  $\nu_4$  vibrational mode<sup>12</sup> of  $\text{CH}_3\text{Cl}$  is  $1455 \text{ cm.}^{-1}$ . That this mode characterizes the methylene group rather than the particular halide selected is evident from the fact that the  $\nu_4$  mode is more nearly constant throughout the methyl halide series than any other mode (it is 1440 for methyl iodide). Clearly, it is the mode most likely to lead to oxidation via the postulated free radical.

### Metal Oxide Vibrations

As in the previously reported study<sup>6</sup> of ethylene reactions, the catalyst is considered the vibrating metal oxide rather than the metal ion. According to the principle, a catalyst must form with one of the reactants (the oxygen) a bond whose vibration frequency coincides with the frequency of the most potent mode ( $\nu_4$ ) of the other reactant. With the objective of revealing a correlation between metal-oxygen bond vibrations and the  $\nu_4$  mode, a tabulation of the more common oxides and their frequencies was made from the spectroscopic data of Jevons<sup>13</sup> and of Pearse and Gaydon<sup>14</sup> by the methods already described.<sup>6</sup> TABLE 1 lists the fundamental frequency and the first overtone for the oxides.

TABLE 1  
VIBRATION FREQUENCIES OF VARIOUS OXIDES

Oxide	Fundamental	Overtone
Silver	484	960
Aluminum	964	1915
Chromium	884	1757
Chromium*	732	1446
Iron	872	1733
Manganese	832	1654
Manganese*	749	1477
Lead	716	1422
Vanadium	999	1994
Calcium	848	1680
Calcium*	737	1467

\*Excited electronic state.

Silver and aluminum have been shown to catalyze an oxidation and hydration, respectively, of ethylene<sup>6</sup> in which the frequency of the potent mode was  $950\text{ cm.}^{-1}$ . They do not coincide at all with the autoxidation of linseed oil. Chromium fulfills the requirement of synchronization, but fails to comply with the first demand made of a drier, namely, that it readily revert to the lower oxidation state after transporting the oxygen to the substrate. Iron also suffers from this deficiency.

The existence of a manganese vibration frequency in the proper region for drier activity is interesting in that an excited electronic state is involved. The manganous ion has the electronic configuration  $3d^5$  and would not be expected to participate in oxidations in which this favored configuration is destroyed.<sup>5</sup> Once this electronic arrangement is broken up by elevation of an electron to a higher level, manganese meets both the electronic and vibrational requirements of a catalyst. Lead and calcium fit well into the picture, but for different reasons. Lead is a well-known primary drier in that it can be used to assist the oxidation, but its activity is low, perhaps because the bulky lead atom slows down the vibration below the most effective range. The calcium-oxygen bond appears to possess the right frequency and can therefore act as a promoter, provided an oxidation catalyst is present to carry the burden of the reaction. Both lead and calcium are used in conjunction with other metal soaps in oleoresinous systems.

By analogy, iron should be active in an excited electronic state. Spectroscopic data were not available for this element, but its efficiency as a drier at high temperature indicates that it follows the expected trend. Cobalt, the most active conventional drier, could not be included in this study owing to the absence of spectroscopic data. Since the square of the vibration frequency depends directly on the force constant and inversely on the mass, the frequency for the  $\text{Co}^{+2}\text{-O}$  bond should be significantly less than for  $\text{Fe}^{+2}\text{-O}$ , for the iron adheres to oxygen more tenaciously than does cobalt, and consequently prefers the +3 oxidation state. Conceivably, the first overtone could approach the 1450 figure for the deformation of the tetrahedron.

### *Summary of Linseed Oil Catalysis*

The attachment of an oxygen molecule to an unsaturated fatty acid involves the displacement of a hydrogen atom. At first, one might inquire whether the hydrogen atom left before the entry of the oxygen (Sn-1), or whether the approaching oxygen forced the hydrogen away by effecting a Walden inversion on the alpha carbon tetrahedron (Sn-2). Neither of these mechanisms requires a free radical as an intermediate.

In the first case, a primary ionization would have taken place, and



the mode of vibration that would lead to reaction would be one of the C-H stretching modes; in the second case, the attack of the oxygen most likely would depend on how well the approaching free vibrator could synchronize its oscillations with that of the carbon atom at which it was directed (perhaps to the C-C bond). Neither of these alternatives was found acceptable from the vibration point of view or from considerations of oxidation as an ionic reaction.

A successful interpretation of the oxidation of linseed oil leading to an understanding of the role of the alpha carbon as a point of attack and of the catalyst for the reaction has been based on the vibration frequency of the bending mode for  $\text{CH}_3$ , which enables two of the hydrogens to assume  $90^\circ$  angles with each other and with a third heavy portion of the molecule. This interpretation has been satisfactory from the standpoints of accounting for the ability of certain catalysts to spearhead the reaction, and utilizing the requirement that free radical formation involves the temporary assumption of the  $p^3$  bond structure. In addition, the role of auxiliary catalysts has been explained.

The explanation of catalysis on the basis of quantum mechanical resonance and molecular vibrations complements an earlier concept that the electronic configuration of the central metal atom of a drier must permit reversible unions with oxygen to occur with a low potential energy barrier.

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